Chapter 6

SUMMARY AND CONCLUSION

Nowadays, scientific improvement agrees to influence and examine the properties of new materials and is changing the energy storage systems. Electrolytes are everywhere and essential in all electrochemical devices and their basic function is to transfer the charge carriers between the electrodes. However, polymer based electrolytes offer high ionic conductivity and has potential application in batteries and fuel cells etc. The traditional polymer electrolytes uses alkali metal salts as ion conducting agent, meanwhile, new ion conducting electrolytes are prepared with ionic liquid. There are limited numbers of literature in sulfoniumand phosphonium ionic liquid based polymer electrolytes in lithium battery research are available. This focuses the attention of many researchers in to the ionic liquid based system.

In the present investigation, a systematic study has been performed based on PVdF-co-HFP polymer. The objective of the present work has focused on the preparation and characterization of ionic conducting polymer electrolyte using alkali metal salt and ionic liquid for the application in the lithium battery. The polymer electrolyte samples have been prepared using the conventional solution casting technique, which is the preferred for its simplicity. For comparison, alkali salt based polymer electrolyte, sulfonium and phosphonium ionic liquid based electrolytes have been prepared and characterized in the viewpoint of their physical and electrochemical properties.

X-ray diffraction analysis has been used to find out the structure and crystalline nature of the material. The complexation between the polymer matrix and its constituents has been analysed from the Fourier-Transform Infraredand Raman spectroscopy techniques. The ionic conductivity of the polymer matrix is an
important parameter and gives the particular potential application in lithium secondary batteries, which is calculated by the AC impedance technique. The porous nature of the surface of prepared electrolytes has been analyzed using scanning electron microscopy and atomic force microscopy techniques. The thermal stability has been determined using TG/DTA analysis. The anodic stability, cyclic reversibility, and discharge capacity were analyzed respectively using linear sweep voltammetry, cyclic voltammetry and charge-discharge studies for the Li/PE/LiFePO₄ cell couple.

In order to understand the role of lithium cation, an attempt has been made to prepare the solid, gel and composite polymer electrolytes using PVdF-co-HFP with LiN (CF₃SO₂)₂ via solution casting technique. Initially, the solid polymer electrolytes were optimized in view of its ionic conductivity value at room temperature and 80 wt% of PVdF-co-HFP and 20 wt% of LiN (CF₃SO₂)₂ has exhibited high ionic conductivity of 1.93×10⁻⁵ S/cm at 303K. A drop in conductivity value has been noticed at higher concentration above 25 wt% of LiN (CF₃SO₂)₂ salt. This is due to the effect of higher amount of lithium salt forms ionic aggregation such as ion doublets and triplets, which restricts the polymer segmental motion. From the above studies, three concentrations of high ionic conducting SPE have been chosen to prepare GPE. The gel polymer electrolytes have been optimized with ethylene carbonate (EC) and propylene carbonate (PC) plasticizers in 1:1 ratio. The high dielectric constant of plasticizers dictates the complete dissolution of the charge carriers and leads to higher ionic conductivity. But, the higher content of plasticizers leads more dispersion of charge carriers in polymer matrix and result a drop in conductivity. From the AC impedance studies, it is observed that the conductivity has been increased by two orders of magnitude (1.72×10⁻³ S/cm at 303K) by the addition of plasticizers. It is
strongly supported by the other characterization techniques such as SEM, TG/DTA, etc. The optimized ratio (80:20) of PVdF-co-HFP:LiN(CF$_3$SO$_2$)$_2$40 wt%- EC+PC 60 wt% was subjected for electrochemical studies. The electrochemical stability of the electrolyte (4.2 V) has been confirmed using Linear Sweep Voltammetry (LSV). It also possesses a discharge capacity of 117 mAh/g for the cell couple Li/PE/LiFePO$_4$ at 0.1C. The Zirconium dioxide based fillers were optimized with the GPE(PVdF-co-HFP:LiN(CF$_3$SO$_2$)$_2$40 wt%- EC+PC 60 wt%). The inorganic filler particle present in the polymer matrix enhances the ionic conductivity and maximum ionic conductivity value of $4.46 \times 10^{-3}$ S/cm has been obtained for the sample K2 with 6 wt% of ZrO$_2$. Discharge capacity of 126 mAh/g has been obtained for the coin cell containing Li / CGPE / LiFePO$_4$ at 0.1 C rate.

The ionic liquid has unique property such as higher ionic conductivity, non-flammable, non-volatile and low vapour pressure. In general, ionic liquid has high ionic conductivity as well as high thermal stability and used as an electrolyte medium in many electrochemical devices. In the view of attaining higher conductivity with environmental friendly nature, the sulfonium ionic liquid SE$_3$TFSI has been chosen in place of alkali metal salt. Five different combinations of PVdF-co-HFP and SE$_3$TFSI have been prepared using solution casting technique. Among them, 75:25 wt% of PVdF-co-HFP and SE$_3$TFSI has higher ionic conductivity of $6.93 \times 10^{-5}$ S/cm at room temperature. It is found that higher the IL content, higher the conductivity, which is due to more amount of charge carriers and produces flexible network. The maximum thermal stability of 240 °C supports the results obtained in the AC impedance studies. The optimized sample PE-IL5 has been subjected for electrochemical studies such as LSV, CV and charge/discharge. The electrolyte decomposition has been observed around 4.4V, which is evidenced from LSV and
cyclic voltammetry provides the electrochemical window of the prepared electrolyte. An appreciable discharge capacity of 133 mAh/g has also been obtained for PE-IL5 electrolyte containing Li/LiFePO₄ cell couple up to ten cycles.

In view of enhancing the conductivity of the above SPE, an attempt has been made to prepare the polymer electrolyte with different plasticizer ratios with and without LiTFSI salt. The maximum ionic conductivity of $1.12 \times 10^{-3}$ S/cm at 303K has been obtained for PVdF-co-HFP (75):SeT₃TFSI (25) + EC+PC (60)wt%. The inclusion of plasticizers induces the polymer chain flexibility and reduces the viscosity of ionic liquids. However, the lithium salts added into IL based gel polymer electrolytes shows a higher degree of crystallinity. Strong anodic stability of 4.67 V has been viewed from the LSV. There was a flat and stable voltage plateau and first discharge capacity of 138 mAh/g were noted with working voltage of 3.4 V.

The Titanium dioxide (TiO₂) has been added in the present IL based gel polymer electrolyte. In the meantime, the addition of inorganic fillers increases the ionic conductivity of the IL based GPEs. With the chosen ratio of(PVdF-co-HFP-SeT₃TFSI-EC/PC (30-10-60) wt%) different amounts of TiO₂ fillers were optimized. According to the results obtained from the complex impedance plot, 6 wt% of TiO₂ based sample has higher ionic conductivity of $3.42 \times 10^{-3}$ S/cm at 303 K. Higher content of TiO₂ reduces the conductivity due to the formation of the aggregation. An electrochemical stability of 4.62 V and discharge capacity of 145 mAh/g have been observed for the coin cell containing Li / CGPE / LiFePO₄ at 0.1 C rate.

The sulfonium cation present in the IL reacts with the metal electrode and reduces its electrochemical performances. In order to reduce the hindrance present in the sulfonium based IL, an attempt has been made to prepare polymer electrolyte with phosphonium ionic liquid ([P₁₄₅₆₆][TF₂N]). Here the solid, gel and composite
polymer electrolytes were prepared and characterized. Initially, the solid polymer electrolyte, 75-25 wt% of PVdF-co-HFP - [P₁₄₅₆₆₆][Tf₂N] exhibits better performances with 3.209×10⁻⁶ S/cm, while adding the plasticizer into the optimized system, PVdF-co-HFP (30 wt%) + [P₁₄₅₆₆₆][Tf₂N] (10 wt%) + EC/PC (60 wt%) the conductivity has been enhanced to 3.40×10⁻⁴ S/cm at 303 K. The addition of plasticizer results wide working voltage with reduced thermal stability. Without plasticizer the electrolyte possesses discharge capacity of 139 mAh/g, and thermal stability of 500°C. The PVdF-co-HFP + [P₁₄₅₆₆₆][Tf₂N] -EC/PC (60 wt%) exhibits thermal stability up to 265°C, the wide electrochemical window of 5V and discharge capacity of 146 mAh/g at 0.1C rate.

In the perspective to achieve high conductivity, different ratios of TiO₂ filler has also been incorporated with PVdF-co-HFP / [P₁₄₅₆₆₆][Tf₂N] / EC+PC. The maximum ionic conductivity of 1.15×10⁻³ S/cm at 303K has been obtained for 6wt% of filler content based sample. The electrochemical stability is up to 5.2V which is confirmed from LSV. The CGPE with 6wt% of TiO₂ produces excellent discharge capacity of 149 mAh/g at 0.1C rate.

On summarizing the above results, the polymer electrolyte based on PVdF-co-HFP (as a host) has been prepared and characterized with Li/PE/LiFePO₄ cell couple. The Lithium cation (LiTFSI) based SPE exhibited ionic conductivity of 1.93×10⁻⁵ S/cm at 303 K, whereas in GPE (60 wt% of EC and PC), the ionic conductivity value has been increased to 1.72×10⁻³ S/cm at 303K and exhibits a discharge capacity of 117 mAh/g at 0.1C rate. When incorporating 6 wt% of dispersoid (ZrO₂) into the CGPE, ionic conductivity has been increased to 4.46×10⁻³ S/cm at 303K, which is higher than the solid and gel based polymer electrolytes. It exhibits a discharge capacity of 126 mAh/g. In order to improve the electrochemical properties of electrolytes, the
incorporation of ionic liquid was tried in the polymer matrix in absence of alkali salts. The sulfonium cation based SPE possesses ionic conductivity of $6.93 \times 10^{-3}$ S/cm at 303 K and offers discharge capacity of 133 mA/g at 0.1C. The ionic conductivity value has been increased to $1.13 \times 10^{-3}$ S/cm at 303 K in GPE and exhibited a discharge capacity of 138 mA/h/g. However, the addition of LiTFSI salt in ILPE system, reduces the conductivity value to $4.26 \times 10^{-4}$ S/cm at 303 K. The sulfonium cation based CGPE possessed ionic conductivity value of $3.42 \times 10^{-3}$ S/cm at 303 K with an initial discharge capacity of 145 mA/h/g. To rectify the corrosion effect of sulfonium cation, phosphonium cation based ILPE has been prepared. The SPE and GPE based on phosphonium cation shows an ionic conductivity value of $3.2 \times 10^{-6}$ S/cm and $3.4 \times 10^{-4}$ S/cm at 303K respectively. The optimized gelled sample revealed an excellent discharge capacity of 146 mA/h/g. As from the CI plot the prepared CGPE film based on phosphonium cation has conductivity value of $1.15 \times 10^{-3}$ S/cm at 303K and initial discharge capacity of 149 mA/h/g at 0.1C rate. Hence, the phosponium based CGPE electrolytes exhibits better performances among the systems studied and this could be used as a potential candidate for the lithium battery fabrication. Further, the studies of ionic liquid based polymer electrolyte for various device applications are in progress.